Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

REMOTE MEASUREMENT OF METHANE IN COAL MINES: A REVIEW

B.W. Konda, R.C. Mitchner and A.B. Hollinger

February 1987

This document is an unpublished interim report prepared for review for discussion and reporting purposes. rec... the opinions of ... (CANMET)

Ce document est un rapport ... approuvé et rédigé ... de ... documentation ... scientifique autre de ... du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

19 pp

ENERGY RESEARCH PROGRAM
COAL RESEARCH LABORATORIES
DIVISION REPORT ERP/CRL 87-8(TR)

MICROMEDIA

REMOTE MEASUREMENT OF METHANE IN COAL MINES: A REVIEW

by

B.W. Konda*, R.C. Mitchner** and A.B. Hollinger***

ABSTRACT

The report outlines the need for a device to measure methane concentrations remotely in underground coal mines. It goes onto describe briefly the analytical techniques using electromagnetic radiation that have been used to measure the atmospheric pollutants remotely. Raman scattering and differential absorption techniques are examined for their suitability in the development of a portable and permissible methane measuring instrument.

---

*Mine Environment Scientist, Cape Breton Coal Research Laboratory, CRL, CANMET, Energy, Mines and Resources Canada, Sydney.

**Applications Engineer and ***Chief Scientist, Moniteq Ltd., Concord, Ontario.

DOSAGE À DISTANCE DU MÉTHANE DANS LES MINES DE CHARBON : UN APERÇU

par

B.W. Konda*, R.C. Mitchner** et A.B. Hollinger***

RÉSUMÉ

Le rapport souligne la nécessité de disposer d'un appareil permettant de déterminer à distance la concentration de méthane dans les mines souterraines de charbon. Il poursuit en décrivant brièvement les techniques analytiques faisant appel au rayonnement électromagnétique qui ont été utilisées pour doser à distance les polluants atmosphériques. Il examine les techniques de diffusion Raman et d'absorption différentielle, en vue d'établir dans quelle mesure elles peuvent être appliquées dans un appareil portatif, utilisable sous terre, permettant de mesurer les concentrations de méthane.

---

*Scientifique de l'environnement minier, Laboratoire du Cape Breton, Laboratoires de recherche sur le charbon, CANMET, Énergie, Mines et Ressources Canada, Sydney.

Ingénieur des applications et * Scientifique principal, Moniteq Ltd., Concord (Ontario).

CONTENTS

	Page
ABSTRACT	1
RESUME	iii
INTRODUCTION	1
DETECTION TECHNIQUES	2
Raman Scattering	3
Absorption Techniques	5
RANGING TECHNIQUES	8
Triangulation	8
Time of Flight	9
EXPERIMENTAL SYSTEMS	11
FUTURE DEVELOPMENTS	13
CONCLUSIONS	13
REFERENCES	14

TABLES

No.		Page
1.	Comparison of cross-sections of different detection processes for methane at S.T.P.	3
2.	Methane cross-sections relative to the Q-branch of the nitrogen fundamental	4
3.	Summary of maximum permissible exposure (MPE) for direct ocular exposure at selected wavelength regions for a one second exposure. Extracted from ref. 2. Pulse widths of approximately 1 ns are assumed	5
4.	Methane absorption coefficients	6

FIGURES

No.		Page
1.	Atmospheric transmission from 0.2 to 15 μm. Shaded areas represent areas of low transmission, ref. 3	7
2.	Schematic of triangulation technique, ref. 4	9
3.	Typical arrangement for time of flight, ref. 5	10

INTRODUCTION

Methane in underground coal mines is a known major safetv hazard and is responsible for most coal mine explosions. The permitted levels of methane concentration in the mine air are stipulated by regulations and the need to measure it accurately has long been recognized. During the past three decades, researchers have developed and demonstrated a wide variety of portable hand-held instruments for measuring methane in mine air. However, all methane monitors available at the present time for use in underground coal mines require that a sample be delivered to the detection cell. Most of these instruments may be used in a remote sense by the use of extension probes, sampling pumps, aspirator bulbs, tube bundles, etc. which transfer the sample from the collection point to the detection instrument or as in most of the modern remote (so called) environmental monitoring systems, the sensor is positioned within the area to be analyzed and the signals generated are transmitted by means of telemetry to a computer in a control station. In all these cases a physical sample is delivered to the sensor.

Remote measurement as envisaged by the authors is a situation in which a portable hand-held measuring device detects and measures methane concentrations at some distance, say 3m to 30 meters. This would allow the determination of methane concentrations in the inaccessible areas in the mine such as roof cavities, open gob areas, sections of roadways that are temporarily unfit to travel before repair, unsupported areas in shortwall and longwall faces, methane layers in high roadways, etc.

Analytical techniques such as LIDAR (light detection and ranging) and differential absorption LIDAR (DIAL) have been used to measure remotely the atmospheric pollutants where distances are large (kilometers) and levels of concentrations are relatively low. A review of these techniques and their applicability and adaptability to measure methane in underground coal mines where the distances of interest are much shorter and the levels of concentration to be detected are much higher is the purpose of this paper. It is recognized that the development of a portable and permissible instrument for use in underground coal mines requires miniaturization and substantial modifications to the equipment designed for surface use.

DETECTION TECHNIQUES

The remote measurement techniques used to detect and measure atmospheric constituents such as methane can be classified into three categories (1):

1. Absorption: molecular species are often characterized by their absorption of radiation at specific wavelengths. Although not all species exhibit a suitable absorption spectra, methane is characterized by several strong absorption features in the infrared region of the spectrum.
2. Raman Scattering: when a Raman active molecule is exposed to radiation at a specific frequency, a small portion of the incident radiation is scattered at a different frequency. Such molecules are characterized by the degree to which the incident radiation is shifted in wavelength. Methane is a Raman active molecule and is characterized by several Raman shift frequencies.
3. Fluorescence: when certain molecules are exposed to radiation, a portion of the radiant energy is emitted at several wavelengths which are characteristic of that molecule. Unlike Raman scattering, the fluorescence emission occurs across a relatively large bandwidth and is independent of the incident frequency, other than it will occur only at longer wavelengths.

A measure of the efficiency of these processes is found in their respective optical cross-sections. A comparison of the optical cross-sections for each of the techniques is shown in Table 1. In general, Raman scattering techniques have relatively small optical cross-sections (comparatively low signals) while absorption techniques are characterized by some of the largest cross-sections. Fluorescence techniques differ in that the optical cross-sections vary with concentration. This change in cross-section is not totally predictable. Consequently, fluorescence techniques are not commonly used for accurate concentration measurements.

Table 1 - Comparison of cross-sections of different detection processes for methane at S.T.P.

Detection Process	Cross-Section (cm^2/sr.mol)
Raman	
-U.V. ___ Visible	1 E-31
Fluorescence	
-U.V. ___ Visible	1 E-14 to 1 E-17
-Infrared	1 E-18 to 1 E-23
Absorption	
-Infrared	1 E-17 to 1 E-21

RAMAN SCATTERING

When a Raman active molecule, such as methane, is exposed to light at a frequency of (Vo), it will produce scattered light at (Vo ± Vi) where (Vi) represents the Raman frequency shift uniquely associated with that molecule. The light which is produced at the frequencies (Vo - Vi) is known as Stokes lines and is generally stronger than the light produced at (Vo + Vi), the anti-Stokes lines. Stokes lines are more useful since they are more intense than anti-Stokes lines.

In choosing which incident frequency to use and which Raman shifted frequency is to be measured, there are several important factors to be considered:

1. Generally, the Raman shifted frequency with the largest scattering cross-section is desired.
2. Ocular and skin exposure safety requirements will determine the maximum source power for the chosen incident frequency.
3. Availability of the source, detector and optical components for the selected frequencies.

The ratio of Raman scattering cross-sections for methane relative to nitrogen are shown in Table 2. The table illustrates that the 2914 cm^{-1}

Raman shift frequency has the largest cross-section and is therefore the preferred choice for monitoring methane.

Table 2 - Methane cross-sections relative to the Q-branch of the nitrogen fundamental

Band	Raman Shift (cm^{-1})	Relative Cross-Section
V1	2914	8.0
V2	3018.9	4.5
V3	1533.3	0.24
V4	1306	0.008

For Raman processes, the differential cross-section varies inversely as the fourth power of the incident wavelength. To maximize the cross-section therefore, the incident wavelength should be chosen as short as possible. Simply stated, operation in the ultraviolet (UV) region is generally preferred to maximize the differential cross-section.

The maximum permissible exposures (MPE) for intrabeam viewing have been summarized in Table 3. The table indicates that the allowable source power is at a maximum in the UV region between 315 nm and 400 nm in the far infrared region above 1.4 μm.

Factors to be considered when selecting optical components and detectors for use with the Raman scattering technique include:

1. The detector must have low noise characteristics and a high gain in order to measure the relatively weak Raman signal.
2. Optical components must not exhibit fluorescence in the methane band.
3. Since the Raman signal is several orders of magnitude less than other sources of radiation such as that due to the scattering of the incident light, filters with extremely high rejection ratios must be employed.

Table 3 - Summary of maximum permissible exposure (MPE) for direct ocular exposure at selected wavelength regions for a one second exposure. Extracted from ref. 2. Pulse widths of approximately 1 ns are assumed

Wavelength (μm)	MPE (J/cm^2)
ultraviolet	
0.200-0.302	0.003
0.305	0.010
0.310	0.100
0.315-0.400	0.560
visible	
0.400-0.700	0.018
near infrared	
0.700-1.050	0.018-0.090
far infrared	
1.400-1000	0.560

The laser source is the single most important factor in determining the size, power requirements and operating specifications of the system. There are, therefore, several factors to be considered when selecting the laser source. These are summarized below:

1. To ensure maximum return signal, the source power should be the maximum allowed by the MPE restrictions.
2. A high efficiency laser should be chosen to minimize the system input power requirements.
3. The laser should be capable of operation in the UV region preferably near 315 nm.

ABSORPTION TECHNIQUES

Absorption techniques can be divided into two general categories. Techniques which measure the absorption of methane at two narrow wavelengths, one on an absorption line and the other at a reference or off absorption line, are referred to as differential absorption techniques. This can be

accomplished in one of two ways. A narrow band source, such as a laser, can be used to generate the on and off absorption line wavelengths. Alternatively, narrow pass-band filters can be used to select the on and off absorption lines emitted from a broad-band source.

A second technique, gas filter correlation, uses a spectrally matched gas filter to measure the absorption due to a specific gas over a relatively large spectral bandwidth. The technique requires the use of a broad-band source which is generally less efficient than a last source.

Several factors must be considered when choosing the wavelength region for use with absorption techniques. The major of these being:

1. Generally absorption lines with large absorption coefficients are chosen to maximize system performance.
2. The chosen wavelength region must be free from interference due to other atmospheric gases.
3. Availablility of the source, detector and optical components for the selected wavelength region.

In addition to two active vibrations in the infrared region (V3 and V4), methane has a number of overtone and combination bands in the near infrared region. A summary of these is shown in Table 4, which illustrates that the V3 band at 3.3913 μm offers the largest absorption coefficient and therefore appears to be a likely choice for measuring methane. However, availability of a suitable source and interference from other constituents in the mine air are other factors that need consideration.

Table 4 - Methane absorption coefficients

Band	Wavelength (μm)	Absorption Coefficient (cm^{-1} atm^{-1})
V3	3.3913	≈8.8
2V3	1.6654	≈0.1
2V3 + V2	1.3312	≈0.05

The selection of an infrared wavelength region in which to measure methane is limited by the transmission of the atmosphere. Water and CO_2 are the major absorbers in the atmosphere and generally limit operation to the following spectral regions (Figure 1):

1. 1.9 to 2.6 μm
2. 3.0 to 4.2 μm
3. 4.4 to 5.4 μm
4. 8.0 to 14.0 μm

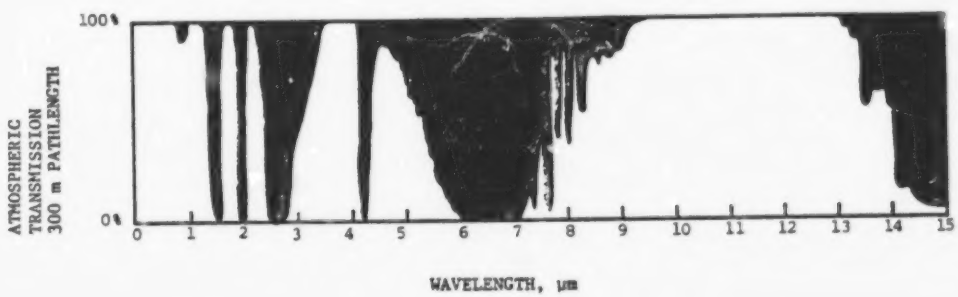

Figure 1 - Atmoshperic transmission from 0.2 to 15 μm.
Shaded areas represent areas of low transmission, ref. 3

Factors to be considered when selecting optical components and detectors for use in the infrared region include:

1. Photovoltaic and photoconductive detectors offer the highest performance in the infrared region. The optimum choice will, however, be determined by the operating wavelength region.
2. Optical components should be selected to maximize transmittance at the operating wavelength region. There are numerous optical components available with suitable characteristics in the regions of interest.

As in the Raman scattering technique, the source itself represents the limiting factor in determining the size and operational characteristics

of an absorption system. The factors to be considered when selecting the source are summarized below:

1. To ensure maximum return signal, the source power should be the maximum as defined by the MPE restrictions.
2. A high efficiency source should be chosen to minimize the system power requirements.
3. In the case of a laser source, whose bandwidth is comparable to methane absorption lines, the laser must have an extremely stable frequency. In addition the laser must be capable of being tuned to both the on and off absorption wavelengths.
4. Use of broad-band sources for differential absorption or GFC techniques is not desirable since a very low percentage of the emitted radiation is actually used in the measurement.

RANGING TECHNIQUES

There are two techniques which can be employed to obtain spatially resolved concentration data. These are:

1. triangulation, and
2. time of flight.

Both techniques can be employed for either Raman scattering or differential absorption measurements.

TRIANGULATION

A typical configuration for a triangulation deployment is shown in Figure 2. Two optical paths are used to make a measurement at a reference volume and a second at a sample volume. Spatial resolution is obtained by differencing the two measurements. There are several points worthy of note concerning this type of arrangement. Firstly, in the case of absorption measurements, the calculation assumes equal gas absorption along the two paths R and R2. Secondly, the optical system must be designed to mechanically scan the entire measurement range. This imposes severe restrictions on

the optics and results in a large package size since it is dependent upon the separation between the source and receiver optics.

The triangulation technique does not, however, impose any additional constraints on the source or detector requirements.

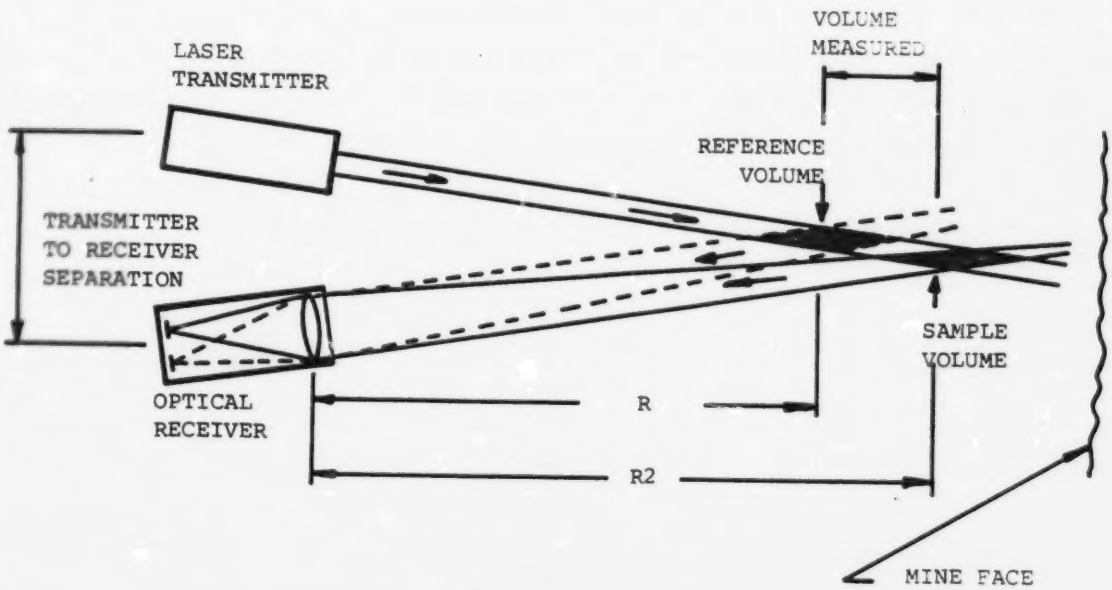

Figure 2 - Schematic of triangulation technique, ref. 4

TIME OF FLIGHT

In time of flight techniques, spatial resolution is achieved by measuring the returned signal as a function of the transit time of the emitted radiation as illustrated in Figure 3. The spatial resolution of the measurement is defined by the source pulse length and the response time of the detector and sampling electronics. As an example, spatial resolution to within 1 m requires that the system be able to resolve the data to within 6 ns. In general, the technique results in a significantly smaller package size since the receiver and source can be aligned collinearly.

The technique, however, imposes severe restrictions on the source pulse length and the detector response time; the impact of which is discussed separately.

To achieve a spatial resolution of 1 m or less the source must be capable of generating pulse lengths of less than 6 ns. For operation in the

UV wavelength region this is possible with sources such as the nitrogen laser, with a pulse length of less than 1 ns or the tripled Nd:YAG, with a pulse length of 5 ns. In the infrared region the only sources which are capable of generating sufficiently short pulse lengths are the semiconductor diodes which, however, are unsuitable for remote methane detection because of their low output power and unstable frequency.

Photomultiplier tube detectors, which operate in the UV region, are characterized by response times of less than 2 ns and are suitable for use with time of flight ranging techniques. The corresponding infrared detectors available with response times of less than 6 ns, are not suitable for the desired application because of their relatively poor sensitivity.

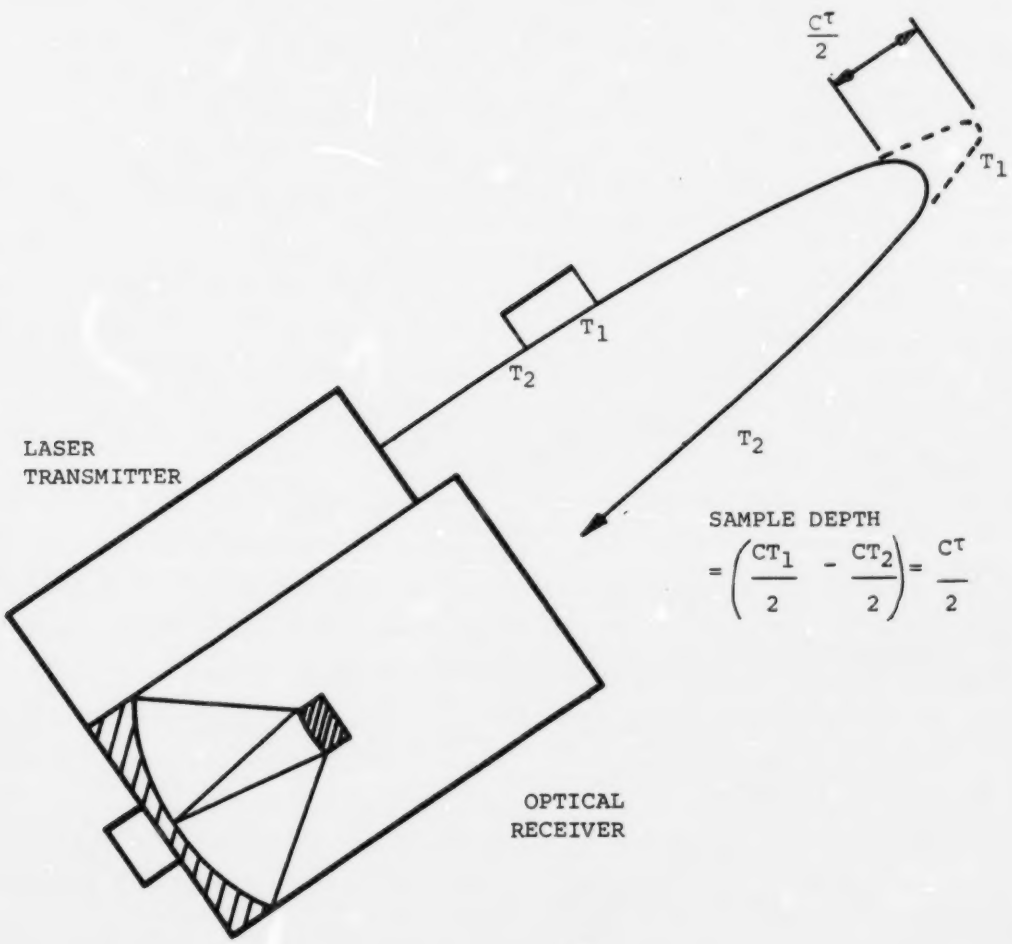

Figure 3 - Typical arrangement for time of flight, ref. 5

EXPERIMENTAL SYSTEMS

The following are representative of the experimental systems that have been developed in the last several years with the ultimate aim of building an instrument to measure methane concentrations remotely in underground coal mines.

Westinghouse

Westinghouse Research and Development Centre has developed a portable system which relies upon the differential absorption technique to measure methane concentrations. The system uses a broad-band, quartz-halogen pulsed flash lamp to provide the necessary source radiation. The light is beamed onto the coalface and a portion of the reflected light is gathered and split into two optical paths for measuring on and off the absorption lines. Two pass-band filters, one centered at 3.37 μm and the other at 2.67 μm, are used to filter the radiation for measurement by two PbSe detectors.

Although the system is capable of measuring integrated path length methane concentrations up to a distance of about 9 m, it has no ranging capabilities. Modifications to include ranging using the triangulation technique would be extensive, requiring replacement of the source, the addition of two detectors and replacement of the signal processing electronics.

Homer Research Labs

Homer Research Labs have developed a prototype system which uses the differential absorption technique to provide spatially resolved methane concentration data. The system uses a tunable ER:YAG laser, operating at 1.6451 μm, as a source of radiation for both the reference and absorption wavelengths. An intra-cavity etalon is used to tune the laser to the two wavelengths. By employing two optical paths, the system is able to measure the reflected radiation in two separate volumes, as described in the Raman scattering section, to provide spatial information. In its current configuration the system is capable of providing the range resolved information only at a fixed distance.

The system has been demonstrated to be capable of achieving the measurement specifications and the resolution requirements at a fixed range. Modifications to include an optical scanning arrangement to allow for

variable range resolution would, however, significantly increase the complexity, size and power requirements of the current system.

MONITEQ Ltd.

MONITEQ Ltd. has developed a sensor for methane detection from an airborne platform. The sensor uses the GFC technique to detect natural gas pipeline leaks by detecting the presence of methane above the earth's surface. The sensor uses the natural radiation upwelling from the earth's surface to measure at the 7.8 μm region. Since an active source is not employed, the system is not capable of providing range information. In addition, the sensor is only capable of measuring low level (less than .1%) methane concentrations.

Operation in an underground coal mine environment would require modifications to the sensor to include a broad band source and implementation of the triangulation technique to provide spatially resolved data. The performance of such a system, however, would not differ appreciably from a similarly modified Westinghouse system. Generally, when high concentrations are to be detected without the need for high specificity, systems which utilize spectral filters, such as the Westinghouse sensor, are preferred over GFC systems.

United States Bureau of Mines

The USBM has developed a laboratory system for measuring methane using the Raman scattering technique. The system uses a pulsed nitrogen laser to emit radiation at a wavelength of 337.1 nm. The returned Raman scattered signal is filtered to eliminate stray radiation and is measured by a photomultiplier tube. The most critical stage in this system is to ensure that adequate filtering is achieved to eliminate stray radiation which is several orders of magnitude larger than the methane signal.

At present the system has only been demonstrated in a laboratory environment and is not portable.

The USBM system has been demonstrated to be capable of achieving the desired measurement and ranging requirements. The system is, however, relatively large and will require extensive engineering to reduce its size and power requirements. Additionally, the signal processing electronics have not yet been developed as an integral part of the entire system.

FUTURE DEVELOPMENTS

Because of the relatively mature state of the technology, major developments in the fields of: optical components, detectors and to a large extent electronics, are not foreseen. Instead, the development of a portable remote methane monitor will depend mainly upon developments in the field of laser sources.

One area of development which is of interest is the semiconductor pumped Nd:YAG laser which has come about from recent developments in semiconductor diode arrays (GaAlAs). These semiconductor arrays, with average optical powers as high as 500 mW and efficiencies of 40%, are being used to replace the relatively inefficient xenon flash lamps currently used to pump the Nd:YAG laser. The result is a relatively efficient laser source which is reasonably compact.

Pulsed Nd:YAG systems which use the semiconductor arrays are under development and should be capable of achieving the required efficiency, size and peak power requirements necessary for remote methane detection using the Raman scattering principle in a time of flight configuration.

CONCLUSIONS

The differential absorption and Raman scattering techniques have the potential for application to detect methane remotely in underground coal mines. However, none of the systems which were being developed satisfy the requirements of a) portability and permissibility, b) ability to measure over the desired concentration range and c) achieve spatial resolution of the concentration data.

It is preferrable to achieve spatial resolution of the concentration data using the time of flight technique since it will result in a less mechanically complex and physically smaller system when compared to a system using the triangulation technique. The technique does, however, impose severe restrictions on the specifications of the source pulse length and detector rise time. Consequently, its use with differential absorption LIDAR operating in the infrared region is limited by the availability of suitable

sources and detectors. Additionally, the Raman LIDAR system has the following advantages over differential absorption LIDAR:

1. Raman technique relies only on the species to be detected for backscattering. Consequently, no other backscatter source need be present to create a return signal. It is often necessary for some retroreflector (coal dust) to be introduced into the absorption LIDAR path.
2. Raman LIDAR system requires only a single frequency transmitter as opposed to a dual frequency source for absorption LIDAR setups.
3. Raman LIDAR can easily be adapted to other potentially hazardous gases by a simple replacement of filters in the receiving optics.

However, before Raman LIDAR could successfully be used in underground coal mines, the problems of portability, high voltages and ultraviolet transmitted light levels for eye exposure need resolution.

REFERENCES

1. CANMET, "Feasibility of using gaspils and other methods of remotely measuring methane in coal mines and preparation of a conceptual design for a suitable instrument"; DSS Contract #14SQ.23440-4-9278; 1986.
2. "American national standard for the safe use of lasers"; Z136-1-1980.
3. Grant, W.B. and Menzies, R.T. "A survey of laser and selected optical systems for remote measurement of pollution gas concentrations"; JAPCA; Vol. 33, No. 3; 1983.
4. Egan, W.D. et al. "Remote differential absorption and scattering measurement of methane near a coal mine working face"; Unpublished report; Bethlehem Steel Corp.
5. Byer, R.L. and Garbuny, M. "Pollutant detection by absorption using mine scattering and topographic targets as retroreflectors"; App. Optics; Vol. 12, No. 7, 1496; 1973.
6. USBM "Dual wavelength light sources"; Contract #H0123031.